Synthesis and Structure of a Diselenido-Bridged Dinuclear Ruthenium Complex $[\{RuCl(P(OMe)_3)_2\}_2(\mu\text{-}Se_2)(\mu\text{-}Cl)_2]$

Jun Mizutani† and Kazuko Matsumoto*† ††
†*Advanced Research Institute for Science and Engineering, and Department of Chemistry, Waseda University,Okubo, Shinjuku-ku, Tokyo 169-8555*
†††*Japan Science and Technology Corporation, Honcho, Kawaguchi, Saitama 332-0012*

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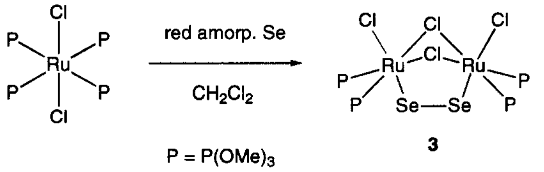
A diselenido-bridged dinuclear ruthenium complex, $[\{RuCl(P(OMe)_3)_2\}_2(\mu\text{-}Se_2)(\mu\text{-}Cl)_2]$ was synthesized by the reaction of *trans*-$[RuCl_2\{P(OMe)_3\}_4]$ and red amorphous selenium. A single crystal X-ray structure analysis showed that the topological geometry was the same as that of the disulfido analogue. The Ru–Se and Se–Se lengths are longer than the corresponding ones in the disulfido analogue according to the difference between the covalent radii of sulfur and selenium. Electrochemical measurement indicated that the title complex undergoes electrical reduction and subsequent chemical reaction.

A number of studies have been carried out so far regarding the syntheses, structures, and reactivities of dichalcogenido-bridged dinuclear and multinuclear complexes in relation to the biological and industrial systems.[1] However, most of the works were focused on disulfido systems and less is known for diselenido- and ditellurido-bridged complexes, which is perhaps due to the lower reactivities of selenium and tellurium sources compared with the sulfur analogues.

We previously reported the synthesis of disulfido-bridged dinuclear ruthenium complex $[\{RuCl(P(OMe)_3)_2\}_2(\mu\text{-}S_2)(\mu\text{-}Cl)_2]$ (**1**),[2] and revealed that its derivative $[\{Ru(P(OMe)_3)_2(MeCN)_3\}_2(\mu\text{-}S_2)](CF_3SO_3)_4$ (**2**)[2] showed novel reactivities.[3,4] For example, **2** activates the carbon–hydrogen bond of acetone to form a carbon–sulfur bond on the disulfido bridge.[4a] If the selenium or tellurium analogue of **2** also shows such reactions towards organic molecules, that would be preferable for organic synthesis, since carbon–selenium and carbon–tellurium bonds are expected to be weaker than carbon–sulfur bonds and it may be easier to remove the organic moieties from the complexes to convert them to new compounds. In pursuit of such systems, we have been making attempts to synthesize the selenium and tellurium analogues of **1** and **2**. In this report, we describe the synthesis and structure of the selenium analogue of **1**, $[\{RuCl_2(P(OMe)_3)_2\}(\mu\text{-}Se_2)(\mu\text{-}Cl)_2]$ (**3**).

In the previous report,[2] the disulfido complex **1** was synthesized by the reaction of *trans*-$[RuCl_2\{P(OMe)_3\}_4]$[5] with excess amount of elemental sulfur at ambient temperature. Synthesis of the selenium analogue, $[\{RuCl_2(P(OMe)_3)_2\}(\mu\text{-}Se_2)(\mu\text{-}Cl)_2]$ (**3**) was attempted with the method for **1**, *i.e.* by use of *trans*-$[RuCl_2\{P(OMe)_3\}_4]$ and metallic gray selenium powder. However, this gave no reaction perhaps due to the low reactivity of gray selenium powder. Instead, employment of red amorphous selenium,[6] prepared by the reaction of H_2SeO_3 and hydrazine, led to the successful synthesis of **3** with moderate yield, although refluxing condition was required.

Details of the preparation of **3** are as follows: a suspension of 134 mg (0.20 mmol) of *trans*-$[RuCl_2\{P(OMe)_3\}_4]$ and 158 mg (2.0 mmol) of red amorphous selenium in 40 ml of dichloromethane was refluxed for 48 h to give purple supernatant. After the excess selenium powder was removed by filtration, the solvent was removed under reduced pressure. The resulting purple powder was washed with 30 ml of hexane for three times, and recrystallized from dichloromethane / diethyl ether / hexane to give purple crystals of **3** with the yield of 60 mg (60%).[7] Ultraviolet-visible spectrum of **3** in dichloromethane showed three absorption bands centered at 360, 540, and 850 nm, each of which was red-shifted by 20–110 nm compared with those of **1**. Attempts to synthesize the tellurium analogue have failed so far because the corresponding allotropic form of tellurium is not known.



The molecular structure of **3** was determined by single crystal X-ray structure analysis.[8] The structure is shown in Figure 1.

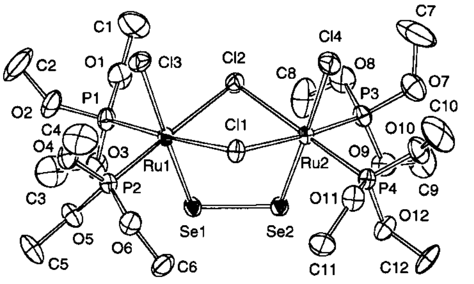


Figure 1. Drawing of the crystal structure of **3**. One of the two crystallographically independent molecules is shown.

The two ruthenium atoms each coordinated by two trimethyl phosphite ligands and a terminal chloro ligand are bound to each other by two chloro bridges and a diselenido bridge. The coordination environment of each ruthenium atom is virtually octahedral. The interatomic distance between the two ruthenium atoms is 3.66 Å av., showing that there is no direct interaction between them. The coordination mode of the diselenido bridge is $\mu\text{-}\eta^1,\eta^1$. Both of the terminal chloro ligands are trans to the selenium atoms, and the trimethyl phosphite ligands are trans to the chloro bridges. Consequently, the topological structure of **3** is the same as that of **1**. The Ru–Se (2.33 Å av.) and the Se–Se (2.27 Å av.) distances are longer by 0.13 Å and 0.30 Å than the Ru–S and the S–S distances in **1**, respectively. These differences are explainable considering the difference of the covalent radii of S and Se (0.13 Å).[9] All other bond distances are almost the same as those in **1**. The Ru–Ru distances (3.66 Å) are longer by 0.08 Å than that in **1**, which is perhaps due to the longer span of the diselenido bridge than that of the disulfide one. Searching the Cambridge Crystallographic Structure Database, we found only one example of dinuclear ruthenium complex having a μ-η^1,η^1-Se_2 ligand: $[\{CpRu(PPh_3)_2\}_2(\mu\text{-}\eta^1,\eta^1\text{-}Se_2)](CF_3SO_3)_2$ (Cp = cyclopentadienyl) (**4**).[10] The geometrical environment around the diselenido ligand in **4** is trans, namely one ruthenium atom is bound on the opposite side of the other ruthenium atom with respect to the diselenido bridge. In contrast, the geometrical environment in **3** is cis, due to the existence of the chloro bridges. Only seven other transition metal complexes having a $M(\mu\text{-}\eta^1,\eta^1\text{-}Se_2)M$ (M = transition metal) moiety whose X-ray structures were determined are known so far: $[(Cp'_2Ti)_2(\mu\text{-}\eta^1,\eta^1\text{-}Se_2)_2]$ (Cp' = methyl cyclopentadienyl),[11] $[(Cp_2TiCl)_2\text{-}(\mu\text{-}\eta^1,\eta^1\text{-}Se_2)]$,[12] $[(Cp'V)_2(\mu\text{-}\eta^2,\eta^2\text{-}Se_2)(\mu\text{-}\eta^1,\eta^1\text{-}Se_2)(\mu\text{-}Se)]$,[13] $[(Cp^*V)_2(\mu\text{-}S)_2(\mu\text{-}\eta^1,\eta^1\text{-}Se_2)]$ (Cp^* = pentamethyl cyclopentadienyl),[14] $[(Cp^*V)_2(\mu\text{-}O)(\mu\text{-}Se)(\mu\text{-}\eta^1,\eta^1\text{-}Se_2)]$,[14] and $[Au_2(\mu\text{-}\eta^1,\eta^1\text{-}Se_n)(\mu\text{-}\eta^1,\eta^1\text{-}Se_2)]^-$ (n = 3, 4).[15] The geometrical environments around the diselenido bridges in all of them are cis as in the present complex **3**, which is perhaps due to the existence of other bridging ligands like chloro bridges in **3**.

The cyclic voltammogram of **3** was measured in dichloromethane with Bu_4NClO_4 as the electrolyte, which is shown in Figure 2(a).

In the first sweep, a redox wave was observed at $E_{1/2}$ = –0.22 V vs. SCE. In the second sweep, however, a new quasi-reversible redox wave was found at E_{pa} = 0.15 V and E_{pc} = 0.08 V. It suggests that the former redox wave is the process of $\mathbf{3}/\mathbf{3}^-$ ($Ru^{III}Ru^{III}/Ru^{II}Ru^{III}$), whereas the latter is the redox wave of the species spontaneously generated from $\mathbf{3}^-$ through a chemical reaction. Accepting this assignment, the redox potential of $\mathbf{3}/\mathbf{3}^-$ is higher by *ca.* 0.09 V than the corresponding potential of the disulfide complex $\mathbf{1}/\mathbf{1}^-$ (–0.31 V, measured under the same condition), indicating that the diselenido complex **3** is more easily reduced than the disulfide complex **1**. Employment of Bu_4NCl instead of Bu_4NClO_4 as the electrolyte significantly decreased the height of only the latter redox waves by *ca.* 1/2. Therefore, it is suggested that the spontaneous reaction involves removal of the chloride ligands on **3**. The cyclic voltammogram of **3** in acetonitrile with Bu_4NClO_4 (Figure 2(b)) showed that the latter redox waves appeared even in the first sweep, indicating that in acetonitrile, which is more coordinating than dichloromethane, the chloride removal from **3** is facilitated. It suggests that acetonitrile substitutes the chloride ligands in **3** giving the similar species as that in dichloromethane. Such behavior was not observed for **1**,[2b] and suggests higher reactivity of **3** for substitution reaction. We are now trying to identify the generated species.

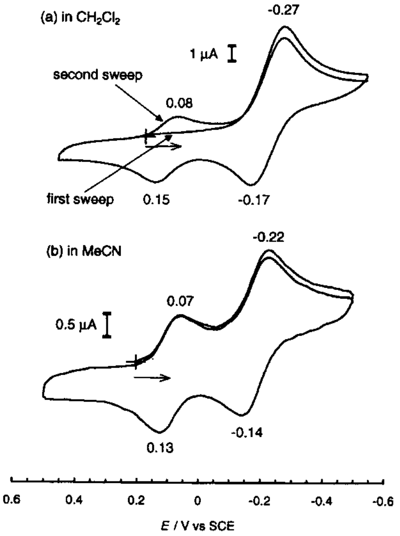


Figure 2. Cyclic voltammograms of **3** in (a) dichloromethane (sample concentration: 1 mM) and (b) acetonitrile (sample concentration: 0.5 mM). Working electrode: Pt, reference electrode: Ag/Ag^+ (calibrated with $FeCp_2/FeCp_2^+$), auxiliary electrode: Pt, supporting electrolyte: 0.1 M Bu_4NClO_4, sweep speed: 200 mV/s.

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7 Anal. Calcd for $C_{12}H_{36}Cl_4O_{12}P_4Ru_2Se_2$: C, 14.4; H, 3.6; Cl, 14.2%. Found: C, 14.4; H, 3.5; Cl, 14.4%. UV-vis (CH_2Cl_2): λ_{max} (nm) (ε, 10^3 $M^{-1}cm^{-1}$) 360(6.9), 540(3.5), 850(8.7). ^{1}H-NMR (CD_2Cl_2): δ = 3.67 (t, J = 5.4 Hz, $P(OCH_3)$), this triplet may actually be an overlap of two doublets).

8 Crystal data for $\mathbf{3}\cdot 0.5H_2O$; formula: $C_{12}H_{37}Cl_4O_{12.5}P_4Ru_2Se_2$, formula weight: 1007.18, triclinic, $P\bar{1}$(No. 2), a = 16.935(3) Å, b = 21.722(3) Å, c = 8.975(2) Å, α = 92.71(1)°, β = 97.58(2)°, γ = 89.79(1)°, V = 3269.0(9) Å^3, Z = 4, D_{calc} = 2.046 g cm^{-3}, μ(Mo Kα) = 37.22 cm^{-1}, diffractometer: Rigaku AFC-7R, measured reflections: 11941, unique reflections: 11516, observed reflections: 9609 ($|F_o| > 2.0\sigma|F_o|$), calculations: teXsan software package (Molecular Structure Corporation), $R(R_w)$ = 0.047(0.066) [$w = 1/(\sigma^2|F_o| + 0.00090|F_o|^2)$], S = 1.47.

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